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LA-UR--86-3107

DE87 000137

TITLE ENERGY TRANSFER, SELF-TRAPPING, AND SOLITONS ON A
NONLINEAR DIMER

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SUBMITTED TO Proceedings of the CNLS Sixth Annual Conference "Nonlinearities
in Condensed Matter," held in Los Alamos, May 4-9, 1986

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Energy Transfer, Self-Trapping, and Solitons on a Nonlinear Dimer

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Abstract

A summary is presented of several results obtained recently concerning the time evolution of a soliton on a lattice. They include the derivation of a Liouville-Von Neumann equation for the density matrix from the discrete nonlinear Schrödinger equation and, for the two-site system, e.g. a molecular dimer, the derivation and explicit solution of a closed nonlinear evolution equation obeyed by the difference of the probabilities of occupation of the two sites. The probabilities are seen to evolve in the form of Jacobian elliptic functions, and a transition from free to self-trapped behavior is seen at appropriate relative values of the intersite interaction and the nonlinearity parameter. Features such as the polaron (or soliton) bandwidth reduction conjectured for the general polaron transport problem are seen to emerge as a consequence. Exact expressions for observables such as the scattering function of relevance to quasi-elastic neutron diffraction experiments are displayed and shown to contain explicit nonlinear characteristics.

The discrete nonlinear Schrödinger equation, which describes a number of phenomena in various fields of physics, may be written as

$$dc_m(t)/dt = -iV(c_{m+1} + c_{m-1}) + i\chi|c_m|^2c_m \quad (1)$$

where c_m is the amplitude for the system to be in state $|m\rangle$, V is the interstate matrix element (assumed "nearest-neighbor" in (1)) describing the linear evolution among the states $|m\rangle$, and χ is the nonlinearity parameter. In the specific system of an electron or exciton in a crystal interacting strongly with phonons or vibrations, $|m\rangle$ denotes the (localized) Wannier state centered on site m , V is proportional to the bandwidth of the bare electron or exciton, and χ is the energy lowering due to polaronic effects, often written as a sum of the products of the vibrational energies of the participating modes and the square of their coupling constants with the electron or exciton. In (1), we have set $\hbar = 1$.

Equation (1) or similar equations have been written down or derived by a variety of people in many different contexts [1-7]. While solutions for its continuum limit are well known [7], analytical solutions for the discrete chain are not available. We have recently found [8] exact time-dependent solutions for (1) for the case of a dimer, i.e. when m can take on values 1 and 2 only, and have applied them [9] to the calculation of experimental observables such as the quasi-elastic neutron scattering function and fluorescence depolarization. A brief description of those solutions and applications follows, our reasons for displaying these results being two. First, they show, in a completely explicit

*Work supported in part by the National Science Foundation under grant no. DMR-850638 and by the Department of Energy under grant nos. 7405/ENG-36 and BES/DMS-86-03-02.

manner, the phenomenon of self-trapping, energy mismatch behavior, polaron/soliton bandwidth reduction and other expected and conjectured features of the evolution described by the equation for the chain of arbitrary length, or generally for a crystal. And second, far from being an overidealized system, the dimer is interesting in its own right and attainable experimentally [10-12]. Calculations for dimer observables are therefore not merely pedagogical in nature but have direct significance in experiments.

Before proceeding further, a comment concerning terminology might prove helpful. Some current usage [2,13] refers to a "soliton" as simply a quasiparticle whose time evolution and motion are described by a nonlinear equation such as (1), independent of the total size of the system. In this usage, phrases like a "soliton in a Wannier or Bloch state" and the idea of a soliton on a dimer are clearly acceptable. In contrast, another usage reserves the term "soliton" for localized, nonlinear solutions only in spatially extended systems (i.e., much larger than a dimer). Those readers who prefer the former usage should look upon the present analysis as that of soliton motion in a dimer. Those who favor the latter terminology should interpret it simply as an investigation of energy transfer in a nonlinear dimer.

The derivation of the Liouville-Von Neumann equation obeyed by the density matrix ρ_{mn} from (1) is straightforward. Equation (1) and its complex conjugate can be combined to give

$$d\rho_{mn}/dt = iV(\rho_{m+1n} + \rho_{m-1n} - \rho_{mn+1} - \rho_{mn-1}) + i\chi(\rho_{mm} - \rho_{nn})\rho_{mn} \quad (2)$$

provided χ is assumed real. We point out that a linear chain with varying site energies would obey (2) with the replacement of the second term $i\chi(\rho_{mm} - \rho_{nn})\rho_{mn}$ by the energy mismatch term $-i(E_m - E_n)\rho_{mn}$, where E_m is the site energy at m . The energy lowering $-\chi\rho_{mm}$ which equals the product of χ and the probability of occupation of site m is thus completely evident in (2). For the dimer, (2) yields

$$d\rho_{11}/dt = -iV(\rho_{21} - \rho_{12}) \quad (3)$$

$$d\rho_{12}/dt = -iV(\rho_{22} - \rho_{11}) + i\chi(\rho_{11} - \rho_{22})\rho_{12} \quad (4)$$

with corresponding equations for ρ_{22} and ρ_{21} . The combination of (3) and (4) and a straightforward calculation involving the elimination of the off-diagonal elements of the density matrix leads to the following closed nonlinear equation for the probability difference $p(t) = \rho_{11} - \rho_{22}$:

$$d^2p/dt^2 = Ap - Bp^3 \quad (5)$$

In the absence of the nonlinearity, i.e. for $\chi = 0$, the coefficient A equals $-4V^2$, B vanishes, and the probability difference p oscillates sinusoidally. In the presence of the nonlinearity, for arbitrary initial conditions, A and B are given by

$$A = (\chi^2/2)p_0^2 - 4V^2 - 2V\chi(\rho_{21} + \rho_{12})_0; \quad B = (\chi^2/2) \quad (6)$$

where the subscript 0 denotes the initial (i.e., $t = 0$) value.

The general solution of (5) and (6) may be written as

$$p(t) = C \operatorname{cn}[(C\chi/2k)(t - t_0) | k] = C \operatorname{dn}[(C\chi/2)(t - t_0) | 1/k] \quad (7)$$

$$1/k^2 = 2 + (1/C^2)[(4V/\chi)^2 + (8V/\chi)(\rho_{21} + \rho_{12})_0 - 2p_0^2] \quad (8)$$

where C and t_0 are arbitrary constants to be determined from the initial conditions, e.g. the values of p and dp/dt at $t = 0$. One can verify directly the general solution (7) by substituting it in (5).

Three consequences of (7) are interesting to explore. The first involves the extraction of the specific form of the stationary states of the system by considering the situation in which all the elements of ρ , and therefore also p , are independent

of t . The second is relevant to the initial condition that only one of the two sites is occupied, and shows a transition from free to self-trapped behavior. And the third is an application of (7) to the calculation of an explicit observable, the scattering function.

To extract the stationary states from (7), we differentiate it twice and equate both dp/dt and d^2p/dt^2 to 0 for all t . This leads to the results that $C = p_0$ and $t_0 = 0$ and to the condition $1/k = 0$. When substituted in (8), this results in

$$(4V/\chi)^2 + (8V/\chi)(\rho_{21} + \rho_{12})_0 = 0, \quad (9)$$

and thence to explicit expressions for the initial values of the density matrix elements. These initial values are, however, the values for all times, since the state under consideration is stationary. Rewriting the elements of ρ in terms of the coefficients of the eigenstates in the site representation, i.e., c_1 and c_2 , we arrive at

$$|c_1| = (1/2)^{1/2} \{1 + [1 - (2V/\chi)^2]^{1/2}\}^{1/2} \quad (10)$$

$$|c_2| = (1/2)^{1/2} \{1 - [1 - (2V/\chi)^2]^{1/2}\}^{1/2} \quad (11)$$

which specifies the stationary states precisely from the general time dependent solution (7). This exercise demonstrates that from our general solution for all times one may recover the stationary dimer results given earlier by Eilbeck et al. [6]. One can obtain (10) and (11) directly, and immediately, from our Eq. (5) by equating its right hand side to zero for $p_0 \neq 0$.

As the second consequence of (7), consider the initial condition that only one of the two sites is occupied initially. The initial probability difference is then $p_0 = 1$ (or -1), and the off-diagonal elements of the density matrix are zero initially. Then,

$$A = (\chi^2/2) - 4V^2; \quad B = (\chi^2/2) \quad (12)$$

The probability difference is given by

$$p(t) = cn(2Vt \mid k = \chi/4V) \text{ for } \chi/4V < 1 \quad (13)$$

if the nonlinear parameter is small enough, but by

$$p(t) = dn(\frac{1}{2}\chi t \mid k = 4V/\chi) \text{ for } \chi/4V > 1 \quad (14)$$

if it is large enough. In the former case the oscillations of the particle are such that it resides equally on both sites but in the latter case it resides more on the initially occupied site. The former case describes free behavior while the latter represents incomplete intersite transfer, i.e. relative trapping as would be characteristic of an energy mismatch. There is thus a transition at $\chi = 4V$. As a function of χ , the detailed behavior is as follows.

For $\chi = 0$, we see that the particle oscillates between the two sites with period π/V . As χ increases, the oscillations of the particle begin to depart from trigonometric behavior. The period of the oscillations of the particle is $T = 2K(k)/V$. It increases as $\chi/4V$ increases. As χ approaches very close to $4V$, the oscillations of the particle show a marked departure from trigonometric behavior: The period becomes enormous as the particle oscillates sluggishly between the two sites. The logarithmic approximation to $K(k)$ is appropriate here and the period of the oscillations of the particle is given by

$$T = (1/V) \ln \{16/[1 - (\chi^2/16V^2)]\} \quad (15)$$

The free particle motion of the particle between the two sites for $\chi < 4V$ described above is depicted in curves (a) and (b) of Fig. 1. When χ equals $4V$, a transition

occurs between this free motion and self-trapped behavior. At the transition, the equalization of the probabilities of the two sites follows exactly a "sech" evolution:

$$p(t) = \text{sech}(2Vt) = \text{sech}(\chi t/2) \quad (16)$$

and the period of the oscillation is infinite. This is shown in curve (c) of Fig. 1.

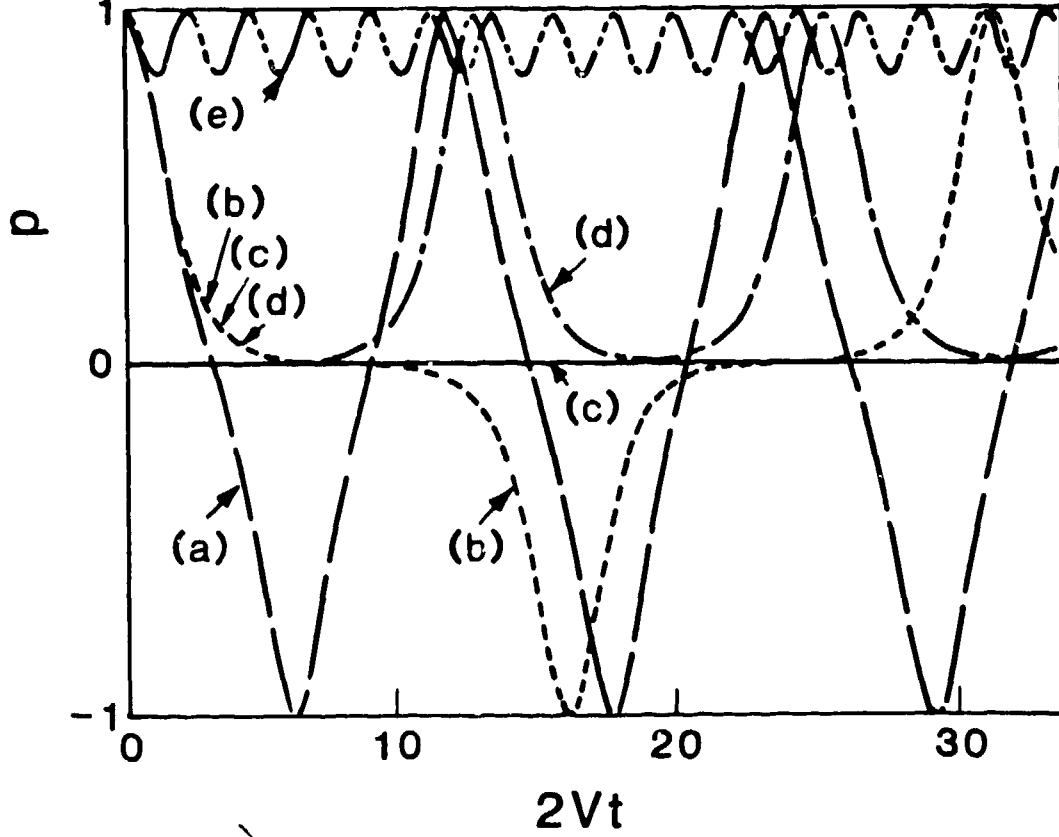


Figure 1. The difference in the probabilities of occupation of the two sites in a dimer plotted as a function of time t (in units of $2V$) for various values of $(\chi/4V)$: (a) 0.95, (b) 0.9995, (c) 1, (d) 1.0001, (e) 1.75. Curves a and b are indicative of free-particle motion, c describes the transition, and d and e represent self-trapping behavior.

As χ increases beyond the transition, the oscillations no longer follow the cn function but are described by the dn function (see (14)). In this region the probability difference never crosses 0. Increasing χ has now two effects: the amplitude of the oscillations decreases and the period also decreases. Far away from the transition, as $\chi/4V$ approaches infinity, the oscillations follow a trigonometric evolution, i.e., can be approximated by

$$p(t) = 1 - (8V^2/\chi^2)\sin^2(\chi t/2) \quad (17)$$

This is precisely the evolution of the probability difference in a linear dimer with a true energy mismatch: the amplitude decreases with an increase in the amount of the energy mismatch. The period of the oscillations is simply $2\pi/\chi$.

This self-trapped particle behavior is depicted in curves (d) and (e) of Fig. 1. In the limit as $\chi/4V$ tends to infinity, the particle is entirely self-trapped as the amplitude (and also the period) of the oscillations becomes zero.

A consequence of our analysis is the clear demonstration that a polaronic/solitonic bandwidth reduction, which represents a lowering of the velocity of the carrier, is a natural outcome of the discrete nonlinear Schrödinger equation in the context of the dimer. Being inversely proportional to the period of oscillation, the reduced

(or effective) bandwidth V_{eff} drops off sharply at the transition as the reciprocal of a logarithm:

$$V_{eff} = V[(2/\pi)K(\chi/4V)]^{-1} \approx V[\pi/\ln\{16/1 - (\chi^2/16V^2)\}] \quad (18)$$

the second equality in (18) being valid close to the transition. Equation (18) establishes unambiguously that a polaronic/solitonic bandwidth reduction does indeed occur.

Finally, as the third consequence of (7), we display the scattering function $S(\omega)$ which describes the intensity of probe particles such as neutrons which would lose or gain energy $\hbar\omega$ when scattered off the quasiparticle (the "moving soliton") as it moves between the dimer sites [9]. The general scattering function $S(q, \omega)$, which involves the (dimensionless) wavevector difference q as well as the frequency difference ω , is, in the case of a dimer, a weighted sum of an elastic contribution and the contribution $S(\omega)$, the weights being determined by the angle of the scattered beam to the line joining the two sites of the dimer [9,14]. The contribution $S(\omega)$ is identical to the Fourier transform of the Van Hove correlation function, which, at high temperatures, becomes identical to $p(t)$, the difference in the probabilities of the two sites for initial single site occupation [15,16]. The Fourier transform of (7) for the initial single site occupation thus gives [9]

$$S(\omega) = \pi[2kK(k)]^{-1} \sum_{n=0}^{\infty} (\text{sech } \omega R_<) [\delta(\omega - \omega_n) + \delta(\omega + \omega_n)] \quad (19)$$

$$S(\omega) = (1/4V) \text{sech}(\omega\pi/4V) = (1/\chi) \text{sech}(\omega\pi/\chi) \quad (20)$$

$$S(\omega) = \pi[2K(1/k)]^{-1} \{ \delta(\omega) + \sum_{n=1}^{\infty} (\text{sech } \omega R_>) [\delta(\omega - \tilde{\omega}_n) + \delta(\omega + \tilde{\omega}_n)] \} \quad (21)$$

for, respectively, the three cases $\chi < 4V$, $\chi = 4V$, and $\chi > 4V$. In (19)-(21), $R_<$ is given by $R_<(k) = K[(1 - k^2)^{1/2}]/2V$, and $R_>(k) = (1/k)R_<(1/k)$. In (19) the summation runs from $n = 0$ to ∞ and $\omega_n = 2V_{eff}(2n + 1)$. In (21), the summation is from $n = 1$ to ∞ and $\tilde{\omega}_n = (n\pi\chi)/2K(1/k)$. While further discussion of these scattering results and an extension for arbitrary temperatures may be found elsewhere [9], we point out here that, as the nonlinearity is increased, (19) exhibits a "march" of the spectral lines towards the origin, (20) represents a collapse of the δ -function lines onto a finite spectrum at the transition, and (21) shows an interesting reemergence of the δ -functions followed by a strengthening of the line at the origin and a weakening, and outward "march", of the other lines. This behavior of the spectrum of the nonlinear undamped dimer as the nonlinearity is changed, resembles very closely, but is not identical to, the phenomenon of motional narrowing exhibited by the spectrum of the linear damped dimer as the damping is changed.

Acknowledgments: This work was supported in part by the National Science Foundation under grant no. DMR-850638 and by the Department of Energy under grants nos. 7405/ENG-36 and BES/DMS-86-03-02.

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